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FINAL REPORT

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**Organic Geochemistry of Seawater Particulate Matter: Final Data
Analysis and Interpretation**

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Abstract

The purpose of this brief grant was to complete the data analysis and preparation of manuscripts resulting from prior ONR-supported research on the organic geochemistry of particulate matter and surface sediments in the Black Sea. That cruise resulted in a unique set of particle and sediment samples, especially in the region of the oxic-anoxic interface. Analysis of lipid biomarkers in these samples has proven invaluable in interpreting the sources and alteration processes which determine the composition of particulate organic matter in the Black Sea. Of particular interest is the in-growth of bacterial biomarkers at the top of the anoxic zone as particles transit the chemocline. Abstracts of the manuscripts prepared to date are given below.

Goal

The long-range goal of this research program has been to characterize the biogeochemical processes controlling the distributions and chemistry of particulate organic matter in the ocean. The specific objective of this grant period was to continue to analyze the data generated from particle and sediment samples collected in the Black Sea and to prepare manuscripts based on these data.

Tasks Completed and Results

Listed below are abstracts for papers published or in press resulting from this ONR-grant.

1. S. G. Wakeham. 1990. Reduction of stenols to stanols in particulate matter at oxic-anoxic boundaries in seawater. *Nature* 342: 787-790. Abstract:

Steroidal alcohols (sterols) are fundamental biochemicals in eukaryotes and are indicators of organic matter sources and transformations in sea water and sediments. Reduction of Δ^5 -stenols, the predominant biogenic sterols, to $5\alpha(H)$ -stanols is primarily an anaerobic microbial transformation. Increased stanol/stenol ratios are used as evidence of this process, for example in Recent sediments where stanol/stenol ratios are higher at lower redox potential. The oxic nature of sea water generally seems to preclude this conversion. However, increased stanol/stenol ratios can also reflect direct biogenic input of stanols or preferential degradation of stenols relative to stanols. Here I report increased $5\alpha(H)$ -stanol/ Δ^5 -stenol ratios in particulate matter at the oxic-anoxic interfaces in the water columns of the Cariaco Trench and Black Sea and attribute them to *in situ* microbial conversion of

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stenol to stanol. The extent of conversion varies with water-column redox potential: little stanol generation occurs under oxic conditions, whereas there is substantial conversion in anoxic waters. These results imply that anoxic waters, particularly near oxic-anoxic interfaces, are important sites of intense alteration of organic matter.

2. S. G. Wakeham. 1990. Algal and bacterial hydrocarbons in suspended particulate matter and interfacial sediment of the Cariaco Trench. *Geochim. Cosmochim. Acta.* 54:1325-1336. Abstract:

Particulate matter samples (<53 μm and >53 μm size fractions) and sediment from the sediment-water interface were collected in the Cariaco Trench, an anoxic marine basin on the continental shelf of Venezuela, and analyzed for hydrocarbons. Concentrations of hydrocarbons were highest (10-20 ng/l) in oxic surface waters (0-150 m) and at the top of the anoxic zone (350-600 m), and were low (3-4 ng/l) in the low oxygen zone above the oxic-anoxic interface (150-250 m) and anoxic bottom waters (600-1150 m). Branched C₂₅-triene and -tetraenes dominated the dyrocarbon distributions in <53 μm particles in the oxic zone, while the isoprenoid C₂₅- and C₄₀-alkanes, 2,6,10,15,19-pentamethyleicosane and lycopane, dominated in the <53 μm particles in the anoxic waters; petrogenic C₁₇-C₄₀ *n*-alkanes dominated the >53 μm particles. Particle size and depth distributions of the hydrocarbons demonstrate the importance of algal hydrocarbons in surface wasters, coupled with increased abundances of bacterial hydrocarbons, especially in the <53 μm particles, in the anoxic zone. These observations illustrate the importance of oxic-anoxic interfaces, even in the oceanic water column, as zones of intense microbial alteration of organic matter and as sources of some of the organic compounds found in sediments.

3. S. G. Wakeham and E. A. Canuel. 1990 Fatty acids and sterols of particulate matter in a brackish and seasonally anoxic coastal salt pond. In *Advances in Organic Geochemistry - 1989; Org. Geochem.* 16. 703-713. Abstract:

Particulate matter and interfacial sediment from a seasonally anoxic coastal salt pond were analyzed for fatty acids and sterols to examine variations in organic sources, and compositional changes across the oxic-anoxic interface in the water column and at the sediment-water interface. Fatty acid distributions in suspended particles varied seasonally and as a function of depth. Fatty acids of algal origin (e.g. 16:3, 16:4, 18:3, 18:4) were abundant in particles in oxic surface waters, but these labile components

were depleted in particles from the anoxic zone which instead were enriched in bacterial fatty acids (e.g. 16:1 Δ^9 , 18:1 Δ^{11} , anteiso-C₁₅). Sterol distributions varied less than fatty acid distributions and particles throughout the water column reflected an upper water algal source with little *in situ* alteration. There was evidence for an *in situ* conversion of Δ^5 -stanols to 5(α)(H)-stanols in suspended particles in the anoxic zone. Sinking particles and the interfacial sediment were compositionally similar to each other, but different from suspended particles. These data reflect differences in particle source, transport and transformation processes occurring in the water column.

4. J. A. Beier, S. G. Wakeham, C. H. Pilskaln, and S. Honjo. 1991. Enrichment in saturated compounds of Black Sea interfacial sediment. *Nature* 351: 642-644.

Abstract:

The sediment/water interface of the ocean should consist of organic compounds produced both in the overlying water column and during early diagenesis. We have found that the uppermost ~ 1mm of sediment samples obtained from the Black Sea are enriched in saturated sterols and fatty acids relative to both suspended particles and underlying sediments. We speculate that either this 'floc' layer contains a microbial community capable of yielding a distribution of compounds that is high in saturated species, or the floc accumulates low-density, fine material enriched in saturated components produced in the water column. Saturated components would thus be formed or concentrated very early during sedimentation and diagenesis. This has important implications for hydrogenation rates in geological environments, and may cast light on the way in which biological materials, rich in unsaturated compounds, become converted into sediments, petroleum and source rocks that contain predominantly saturated compounds.

5. S. G. Wakeham and J. A. Beier. In press. Fatty acid and sterol biomarkers as indicators of particulate organic matter source and alteration processes in the water column of the Black Sea. *Deep-Sea Res.* Abstract:

Fatty acids and sterols were measured in samples of particulate matter and surface sediments in the Black Sea to assess organic matter source and alteration processes in the water column, especially at the chemocline. Fatty acid and sterol distributions in particles in the oxic zone shallower than 100 m reflect their mixed plankton source coupled with aerobic decomposition of organic matter as particles sink. At the oxic-anoxic interface, the residual planktonic fatty acids were supplemented by fatty acids (e.g. iso- and

anteiso-C₁₅ and *C₁₇*, 10-methyl-*C₁₆*, 16:1 ω 7 and 18:1 ω 7) biosynthesized by anaerobic bacteria, most likely sulfate-reducing and photoprophic sulfure bacteria, inhabiting the top of the anoxic zone. The sterol composition changed notably by increased abundances of 5 α (H)-stanols, presumably as anaerobic microbial alteration products of Δ^5 -stanols of planktonic origin. These bacterial biomarker fatty acids and sterols were predominantly associated with the slowly sinking <53 μ m particles, while the more rapidly sinking >53 μ m particles apparently transited the anoxic zone with much less alteration in composition.

6. S. G. Wakeham, J. A. Beier and C. H. Clifford. In press. Organic matter sources in the Black Sea as inferred from hydrocarbon distributions. NATO Advanced Studies Institute volume of Black Sea Oceanography. J. W. Murray and E. Izdar, eds.

Abstract:

Suspended and sinking particulate matter from the water column and sediment and fecal pellets from Unit I sediments were collected in the central basin of the Black Sea for organic geochemical investigations. The hydrocarbon compositions of these samples proved informative for providing information on the sources for the particulate and sedimentary organic matter. Hydrocarbons derived from planktonic, terrestrial, bacterial, and fossil sources can be distinguished. Plankton-derived from planktonic, terrestrial, bacterial, and fossil sources can be distinguished. Plankton-derived hydrocarbons dominated the <53 μ m particles in the oxic surface waters (94% of total hydrocarbons were planktonic, largely from *Emiliania huxleyi*), but an equal mix of planktonic and fossil hydrocarbons was present in the >53 μ m particles. by contrast, <53 μ m particles in the anoxic zone were dominated by hydrocarbons of bacterial origin (76% of total hydrocarbons at 2000 m were bacterial). Large (>53 μ m) particles in the anoxic zone contained equal amounts of hydrocarbons from all four sources. Fecal pellets and sediments contained the greatest contribution of hydrocarbons of terrestrial origin (up to 56% of total hydrocarbons).

7. C. Lee and S. G. Wakeham. In Press. Organic matter in the water column. Future challenges. Mar. Chem. Abstract:

Recent research has greatly changed our knowledge of processes affecting organic matter in the water column. Here we review some of this recent research and suggest several areas which are particularly challenging for future studies. Major areas discussed are newly developed methods of

DOC analysis, the implications of the resulting findings, and the potential significance of organic colloids in seawater. Recent advances in techniques for the analysis of small, labile organic molecules and in radiotracer techniques used to follow rates and mechanisms of biological consumption are also discussed. Ocean-atmosphere transport and photochemical processes can act as both sources and sinks of organic matter in the sea. This is an area where significant progress has been made recently. Finally, we discuss current knowledge of river transport to the oceans and particle sedimentation in the sea as well as some of the limitations on this knowledge.

8. S. G. Wakeham and C. Lee. In Press. Production, transport, and alteration of particulate organic matter in the marine water column. In: *Organic Geochemistry*, M. H. Engel and S. Macko, eds. Elsevier. Abstract:

This paper is a synthesis of recent results for our work and that of others detailing the biogeochemical processes affecting the behavior of particulate organic matter in the water column of the ocean. The discussion includes 1) processes affecting the vertical flux of organic matter sinking through the water column and 2) the many factors which influence the quality of particulate organic matter in the water column.

Papers in Refereed Journals and Books Citing This ONR Grant (inc. those in press)

S. G. Wakeham. 1990. Reduction of sterols to stanols in particulate matter at oxic-anoxic boundaries in seawater. *Nature* 342: 787-790.

S. G. Wakeham. 1990. Algal and bacterial hydrocarbons in suspended particulate matter and interfacial sediment of the Cariaco Trench. *Geochim. Cosmochim. Acta* 54:1325-1336.

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S. G. Wakeham and J. A. Beier. In press. Fatty acid and sterol biomarkers as indicators of particulate organic matter source and alteration processes in the water column of the Black Sea. Deep-Sea Res.

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